

SCIENCE FOR CERAMIC PRODUCTION

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SOLID SOLUTIONS OF SILICON OXIDE IN MULLITE

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An explanation is proposed to account for the possibility of formation of solid solutions of silicon oxide in mullite. The difference in the diffusion coefficients of cations in complex oxides leads to the formation of a solid solution of the oxide containing the cation with the lower diffusion coefficient in the complex oxide and a phase containing the cation with the higher diffusion coefficient or rich in this oxide. Using yttrium or scandium additives, which are chemisorbed on the surface of aerosil (SiO_2 source), it is possible to make the rate of diffusion mass transfer of aluminum cations higher than that of silicon cations and thus obtain a solid solution of silicon oxide in mullite.

Mullite ceramics has a number of valuable properties: low TCLE, high thermal resistance and strength at elevated temperatures (bending strength 150 MPa at 1400°C), low dielectric permeability and dielectric loss tangent and, accordingly, a low loss factor (their product) [1]. Using additives, it was possible to produce high-density ceramics in the $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system with the ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ranging from 3 : 2 to 1 : 2, and its properties were investigated [2]. It was concluded in [2] that a solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ had been synthesized. Phase diagrams have data only on the formation of solid solutions of Al_2O_3 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ [3]. The reason for the formation of sufficiently stable solid solutions of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ was not clear until recently, which cast doubts in the reliability of results.

The purpose of the present study is to provide an explanation for the formation of solid solutions of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

Synthesis of complex oxides is usually performed on the basis of simple oxides or compounds transforming into oxides under thermal treatment. The diffusion rates of cations integrating a complex oxides are usually different, which produces several effects. Let the diffusion coefficient of cations K_1 in a complex oxide be higher than the diffusion coefficient of cations K_2 . When it is synthesized from simple oxides, the reaction front shifts toward the crystal of the oxide with K_1 (the Kirkendall effect) and pores are formed in the same crystal (the Frenkel effect). Furthermore, this leads to γ -nonstoichiometry in the complex oxide. In solid-phase

synthesis from simple oxides with vacancy type of diffusion, a solid solution of the oxide containing the cation with the lower diffusion coefficient (K_2) in the complex oxide is formed, and also a phase consisting of the oxide with the cation that has the higher diffusion coefficient (K_1) or enriched with this oxide [4]. The presence of the second phase and the solid solution concentration have an effect on all sensitive processes and properties in ceramics: sintering, electrophysical characteristics, high-temperature creep, etc.

The deviation from stoichiometry in a complex oxide depends on the degree of nonequilibrium of its synthesis. The higher it is, the more the solid solution synthesized may differ from a stoichiometric complex oxide [4]. This makes it possible to obtain solid solutions with a higher content of the oxide containing cation K_2 compared to conditions approaching equilibrium. Such solid solutions are metastable and disintegrate when exposed at high temperatures.

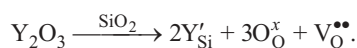
It is known that in the synthesis of mullite from oxides, the mass transfer velocity of silicon cations significantly exceeds the velocity of aluminum cations [5]. This leads to the formation of solid solutions of Al_2O_3 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. At the same time, this opens up possibilities of obtaining solid solutions of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. To accomplish this, the mass transfer of silicon cations in the synthesis of mullite should be made slower than that of aluminum cations. This can be accomplished by using additives decreasing the diffusion mass transfer of silicon cations and/or increasing mass transfer of aluminum cations.

Synthesis of mullite in experiments was carried out using aluminum oxide of grade “extra pure”, aluminum chloride of grade “chemically pure”, and industrially produced Aerosil

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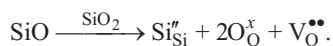
(silica powder) with a specific surface area of 300 m²/g as a source of SiO₂. Aerosil consisted of x-ray amorphous SiO₂ particles sized below 1 μm joined in highly porous aggregates. The additives (scandium or yttrium oxides) were introduced in an amount up to 2 wt.% in the form of aqueous solutions of the respective chlorides. According to the first method, aerosil and aluminum oxide were mixed in milling in an aqueous medium, to which the additive solution was added. According to the second method, a suspension of aerosil and aluminum chloride with the additive introduced were poured or sprayed into a concentrated ammonia solution. Samples were fired in air in a furnace with heaters made of molybdenum disilicide. In the first method, mixtures with Al₂O₃ : SiO₂ ratio equal to 3 : 2 and 1 : 1 were used to mold samples, and then high-density ceramic was obtained after firing combining synthesis and sintering of mullite in a single stage. According to the second method, high-density ceramic was obtained from previously synthesized mullite powder. Synthesis was carried out in air at a temperature of 1200°C.

The reason for the formation of solid solutions of SiO₂ in 3Al₂O₃ · 2SiO₂ is predominant sorption of cations of the additive on aerosil. This is facilitated by the fact that the additive cations have alkaline properties and aerosil has acid properties. The additive incorporates into a solid solution with SiO₂ and creates oxygen vacancies V_O^{••}, which delays the diffusion mass transfer of silicon cations [6]. This can be illustrated by a quasischemical reaction



Predominant chemisorption of additive cations on aerosil is confirmed by analysis of compositions, to which 10 wt.% Sc₂O₃ was introduced. Petrography studies and x-ray phase analysis data corroborate the formation of Sc₂O₃ · SiO₂ (Fig. 1).

The deceleration of the rate of diffusion mass transfer and an increasing concentration of oxygen vacancies offers a reason for the formation of mullite of composition Al₂O₃ · SiO₂ during its synthesis in a reducing medium [7]. The formation of oxygen vacancies can be represented as the formation of a solid solution of SiO in SiO₂:



In these conditions the mass transfer of silicon cations becomes less intense than that of aluminum cations, which creates prerequisites to the formation of solid solutions of SiO₂ in 3Al₂O₃ · 2SiO₂.

The process of prevalent sorption of additive cations on aerosil is intensified in an alkaline medium developed by concentrated ammonia. Precipitation of aluminum chloride on aerosil (without introducing additives) in an ammonia medium (pH = 9) and in ammonium carbonate (pH = 3) demonstrates significant differences in the behavior of the resulting precipitates under heating. According to the Le

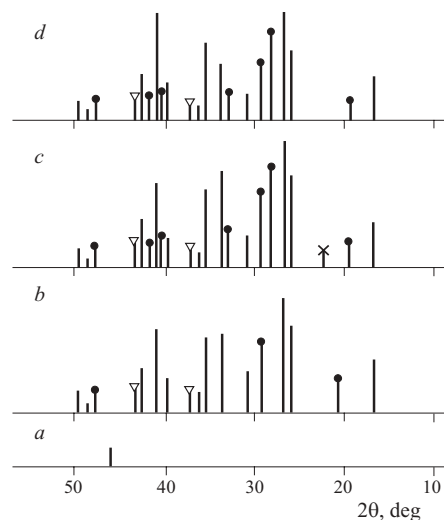


Fig. 1. Diffraction diagram of a mixture of 3Al₂O₃ · 2SiO₂ with 10 wt.% (molar content 34.299%) Sc₂O₃ subjected to heat treatment at temperatures of 1100°C (a), 1200°C (b), 1300°C (c), and 1400°C (d): |) mullite; x) cristobalite; ∇) α-Al₂O₃; ●) Sc₂O₃ · SiO₂.

Chatelier – Brown principle, the more intense is the action on a system (SiO₂ surface), the more intense is the counter-action. The system rearranges itself to maximally oppose the effect. The higher the alkaline properties of the ambient medium acting on the SiO₂ surface, the more acid properties (negative charge value) are manifested by this surface. The isoelectric point for aerosil is within a range of pH = 1.3 – 3.7.

A study of DTG curves of precipitated powders demonstrates that due to chemical reaction between aluminum cations and SiO₂ surface, the strength of their chemical bond to hydroxyl in aluminum hydroxide in the ammonia medium is perceptively lower than in ammonium carbonate. The removal of chemically fixed water from powders precipitated in ammonia is significantly facilitated (the activated energy decreases) [8].

When precipitation was implemented in ammonium carbonate (an acid medium), the relatively low negative charge of the SiO₂ surface resulted in lower chemisorption of aluminum cations on this surface. As a result, after heat treatment at 1200°C the powder (according to x-ray diffraction and petrography data) consisted of γ-Al₂O₃ and α-Al₂O₃, whereas formation of mullite had just started. As for powders precipitated in ammonia in the same conditions, mullite had been formed in them to a perceptible extent. Mullite formation in these powders ended at 1250°C, whereas in powders precipitated in ammonium carbonate it ended only at 1400°C.

Intense chemisorption of aluminum cations on aerosil surface presumably facilitates its incorporation into a solid solution with SiO₂ and formation of oxygen vacancies:



This decelerates to some extent the diffusion mass transfer of silicon cations and brings it closer to that of aluminum.

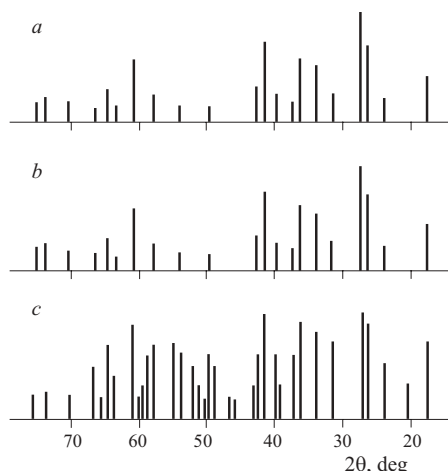


Fig. 2. Diffraction patterns of mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (a), solid solution $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (b), and sillimanite (c).

This leveling of the mass transfer flows of silicon and aluminum facilitates the synthesis of mullite. Consequently, the increased pH of a medium in precipitation (from ammonium carbonate to ammonia) leads to more intense chemisorption of aluminum cations on aerosil, which facilitates the synthesis of mullite (lowers the temperature of synthesis and raises the yield of mullite). All this agrees with the assumption that chemisorption of additive cations predominantly proceeds on aerosil, and not on aluminum oxide or hydroxide.

In sintered ceramics with an $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio equal to 3 : 2 (mullite composition), the crystals had perceptibly different shapes. The mullite crystals from the solid solution had a more isometric shape and a smaller size, in contrast to mullite crystals produced directly from oxides, which had a clearly nonisometric shape. An analysis using an electron microprobe demonstrated that yttrium and scandium additives are predominantly concentrated in the solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and in mullite formed from this solution. An increase in the amount of additive raises the content of the solid solution and, accordingly, of isometric crystals. The size of such crystals becomes smaller as well.

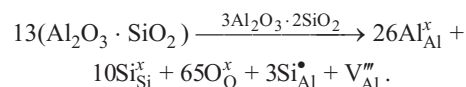
The quantity of additive in the mullite crystals formed directly from simple oxides is low. This is presumably the reason for their nonisometric shape typical of pure mullite crystals (without additives). By the way, the reason for such shape of crystals is most probably the fact that they are obtained via a solid solution of aluminum oxide in mullite. In the course of their growth in sintering these extended crystals loosened the structure and decreased the strength of ceramics.

Solid solutions of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with yttrium and scandium oxide additives had sufficiently high stability. The phase composition of ceramics with an $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio equal to 1 : 1 varied little after its exposure for 40 h at a temperature of 1700°C . Apparently, the rate of its decomposition into mullite and silicon oxide is rather slow. It is surprising that the peak parameters of the solid solutions and

mullite with additives varied insignificantly on diffraction patterns and even in studies using the Guinier camera. Usually formation of solid solutions leads to a perceptible shift of the peak position. This is presumably a specific feature of mullite structure. Additional silicon cations in these structure are found in tetrahedral positions instead of aluminum atoms. A similar phenomenon exists in the sillimanite – mullite series [9, 10]. In this case new x-ray reflection planes do not emerge and the position of the planes existing in mullite does not change.

The diffraction patterns of mullite with yttrium or scandium oxide additive and solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with an ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ equal to 1 : 1 completely coincided in their peaks, but differed perceptibly from sillimanite (Fig. 2). However, a halo was registered in the solid solution in the range of reflection angles $2\theta = 15 - 25^\circ$, pointing to the presence of a vitreous phase. Assuming that SiO_2 is not incorporated into the solid solution with $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, its molar ratio in the mixture should amount to 50%. For verification, samples of mullite and solid solution were milled and treated with hot hydrofluoric acid, which was intended to dissolve SiO_2 that had not incorporated into the solid solution. Powders before and after this treatment were subjected to x-ray phase analysis, petrographic analysis, and weighing. The peaks on the diffraction patterns did not change, but the halo disappeared. Based on the quantity of the phase dissolved in hydrofluoric acid, it was calculated that 37.3% SiO_2 remained in the solid solution with $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Petrography analysis indicated that the phase with an increased content of silica (refraction index $n_g = 1.530 - 1.630$), which had been located at the periphery of mullite grains in the form of interlayers less than $1 \mu\text{m}$ thick, had been dissolved in hydrofluoric acid. A solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with an $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio equal to 1 : 1 should contain 50% SiO_2 .

To confirm the probability of formation of a solid solution without a perceptible modification of mullite lattice parameters and diffraction patterns, formulas of a possible solid solution were calculated. Considering the possibility of solid solution formation in the mullite-sillimanite series [9, 10], it is highly probable that not directly SiO_2 , but precisely sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, dissolves in mullite. It is quite likely that the formation of orthosilicate of the additive facilitates this process. The quasichemical reaction corresponding to the distribution of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ in mullite structure $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, under which a minimum number of vacancies are formed, has the following form:



It is possible to verify the validity of the solid solution proposed here by comparing x-ray density with density obtained by the pycnometry method. The absence of a shift of

the peaks on diffraction patterns shows that the elementary cell size virtually does not change. In this case the ratio of x-ray densities will be equal to the ratio of formula units. To do this, we will take the ratio of molecular mass of the solid solution ($26\text{Al}_{\text{Al}}^x + 10\text{Si}_{\text{Si}}^x + 65\text{O}_{\text{O}}^x + 3\text{Si}_{\text{Al}}^\bullet + V_{\text{Al}}'''$) to the respective molecular mass of mullite $5(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$:

$$2106.52/2130.25 = 0.989.$$

The pycnometric density of the solid solution was equal to $3.10 - 3.13 \text{ g/cm}^3$ depending on the type and quantity of scandium or yttrium oxide, and that of pure mullite was 3.15 g/cm^3 :

$$(3.10 - 3.13)/3.15 = 0.984 - 0.994.$$

Good correlation of calculated values corroborates the probability of formation of solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with an ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ equal to 1 : 1.

Based on the above, it is possible to calculate the ultimate concentration of the solid solution. In the right part of the equation corresponding to five formula units of mullite, three silicon cations $3\text{Si}_{\text{Al}}^\bullet$ are located in the positions of aluminum. Based on these data, it is easy to find the molar content of the solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$:

$$3 \times 100/(3 + 5) = 37.5\%.$$

This values agrees well with the result given above (37.3%) obtained on dissolving SiO_2 that had not reacted in hydrofluoric acid.

Thus, the difference in the rates of diffusion mass transfer (vacancy mechanism) of the cations of oxides that react and form a complex oxide usually at the initial stage leads to the formation of a solid solution of oxide containing the cation with a lower diffusion coefficient in this complex oxide. In synthesis of mullite these are solid solutions of Al_2O_3 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Varying the rates of diffusion mass transfer of oxide cations may alter the situation. Introduction of yttrium or scandium additives into silicon oxide in synthesis decelerates the mass transfer of silicon cations and makes it

possible to obtain a solid solution of SiO_2 in $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Such solid solutions, due to their metastability, gradually disintegrate in the course of exposure at high temperatures. However, such ceramics can function for a long time at lower temperatures, which opens up ways for producing materials with unusual properties. Disintegration of unstable solid solutions is promising as well for obtaining nanostructures. A relatively low rate of diffusion in a solid body facilitates control of the size of emerging nanoparticles.

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